Electron Diffraction Study of 3-Methyldiaziridine

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Summary The molecular dimensions of the diaziridine ring have been measured for the first time in the gas phase by electron diffraction.

THREE-MEMBERED ring compounds containing two nitrogen atoms have been investigated widely.[1] Diazirines are carbene precursors and diaziridines are useful for synthesis of hydrazines. While the structure of diazirine[2] and several derivatives[3,4] is known in the gas phase there is no information on the molecular dimension of the diaziridine ring except one *X*-ray study.[5] As a part of a study on the structures of small heterocyclic systems we report here an electron diffraction study of 3-methyldiaziridine (**1**).

Copper and stainless steel materials are known to decompose diaziridines and, in order to prevent this, the injection system was constructed from nickel. A fine brass nozzle was used which does not disturb the electron beam. The main molecular parameters obtained by Seip's programme[6] are $r_g(1)$[7] and are shown in the Figure. Our study confirms the stereochemistry and ring structure of (**1**) and also provides principal bond lengths for comparison with those of related molecules.

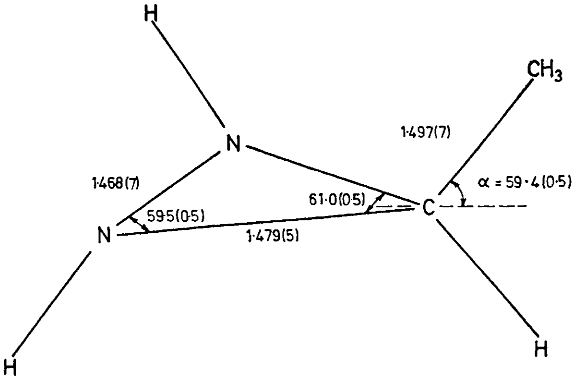

FIGURE. Bond lengths (Å) and angles (°) in the diaziridine ring. Standard deviations (1σ) are shown in parentheses. α is the angle between the C–C bond and the plane of the diaziridine ring.

The N–N bond distance is nearly halfway between that reported for hydrazine[8] [1·449(4) Å] and tetrafluorohydrazine[9] [1·492 (7) Å.] Of most interest is the observation that the C–N bond distance obtained is significantly longer than in NMe_3[10] [1·455(2) Å] and seems to be only slightly affected by the environment, being nearly the same in such different cyclic compounds as diazirine[2] (1·482), ethylenimine[11] (1·475 Å), (**1**) (1·479), azetidine[12] (1·477), and triethylenediamine[13] (1·472).

The C–C bond lengths and the angle α (Figure) are similar to those in several diazirine derivatives.[4]

The hydrogen atoms attached to nitrogen were expected to be *trans* with respect to the three-membered ring and we made no attempt to relax this assumption. This problem is being resolved in our study of 1,2-dimethyldiaziridine which is in progress.

There is an interesting parallel in the ring geometry of cyclopropane,[14] cyclopropene,[15] diazirine,[2] and (**1**). The C–C and C–N single bond distances in saturated and unsaturated compounds remain nearly constant, indicating that the double bond has a negligible effect on the adjacent single bonds. This is unusual for open-chain molecules. In general, the molecular geometry of (**1**) is not unexpected and is very close to those 'reasonable' parameters assumed in LCAO–MO–SCF calculations.[16] However, these results can be contrasted with *X*-ray measurements[5] where nearly regular triangular CN_2 was found with $r(C–N) = r(N–N) = 1·57 \pm 0·05$ Å. We have no explanation to offer for this phenomenon.

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[1] E. Schmitz, 'Dreiringe mit zwei Heteroatomen,' Springer-Verlag, 1967.
[2] L. Pierce and V. Dobyns, *J. Amer. Chem. Soc.*, 1962, **84**, 2651.
[3] J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, 1967, **89**, 5527.
[4] J. E. Wollrab, L. H. Scharpen, D. P. Ames, and J. A. Merritt, *J. Chem. Phys.*, 1968, **49**, 2405; L. H. Scharpen, J. E. Wollrab, D. P. Ames, and J. A. Merritt, *ibid.*, 1969, **50**, 2063; J. E. Wollrab and L. H. Scharpen, *ibid.*, 1969, **51**, 1584.
[5] E. Höhne, *J. prakt. Chem.*, 1970, **312**, 862.
[6] B. Andersen, H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, 1969, **23**, 3224.
[7] L. S. Bartell, *J. Chem. Phys.*, 1955, **23**, 1219.
[8] Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Japan*, 1960, **33**, 46.
[9] M. M. Gilbert, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, 1972, **56**, 1691.
[10] B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, 1968, **64**, 2561.
[11] B. Bak and S. Skaarup, *J. Mol. Structure*, 1971, **10**, 385.
[12] O. V. Dorofeeva, V. S. Mastryukov, L. V. Vilkov, and I. Hargittai, *J.C.S. Chem. Comm.*, 1973, 772.
[13] A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Japan*, 1971, **44**, 72.
[14] K. Hedberg, F. M. Fritsch, and O. Bastiansen, *Acta Cryst.*, 1964, **17**, 538.
[15] P. H. Kasai, R. J. Meyers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, 1954, **30**, 512.
[16] H. Basch, M. B. Robin, N. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, 1969, **51**, 52; R. Bonaccorsi, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta*, 1971, **21**, 17.